

Research Article

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Degradation of AB25 dye in liquid medium by atmospheric pressure non-thermal plasma and plasma combination with photocatalyst TiO_2

Abstract: In this work, degradation of the anthraquinonic dye Acid Blue 25 by non-thermal plasma at atmospheric pressure with and without photocatalyst is investigated. Titanium dioxide (TiO_2) is used as a photocatalyst. The dye degradation by plasma in the presence of TiO_2 is investigated as a function of TiO_2 concentration, dye concentration and pH. The degradation rate is higher in acidic solutions with pH of 2 to 4.3, especially at pH 2, and decreases to $0.38 \text{ mg L}^{-1} \text{ min}^{-1}$ with the increase of pH from 2 to 5.65. A similar effect is observed in basic media, where a higher degradation rate is found at pH = 10.3. The degradation rate increases in the presence of TiO_2 compared to the discharge without photocatalysis. The results show that the degradation of the dye increases in the presence of TiO_2 until the catalyst load reaches 0.5 g L^{-1} after which the suppression of AB25 degradation is observed. The results indicate that the tested advanced oxidation processes are very effective for the degradation of AB25 in aqueous solutions.

Keywords: glow discharge, wastewater, non-thermal plasma, advanced oxidation processes

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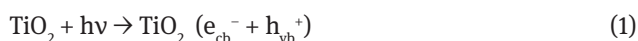
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1 Introduction

The manufacturing processes of textile materials are usually combined with the use of dyes in high concentration. Correspondingly, after the dyeing process, a significant amount of wastewater with intensive color and toxicity is introduced into the aquatic systems. Even a small amount of dye in the water (e.g. $5\text{--}20 \text{ mg L}^{-1}$) is very noticeable. Both the transparency and the gas solubility of the water are affected by this type of pollution. Additionally, some dyes are carcinogenic or mutagenic, and they may also contain different heavy metals which breach environmental standards [1–4]. Recently, several technologies have been developed for environmental pollutant decrease [5–7]. In addition to methods like micro- and nano-filtration [8–10], chemical destruction and ion exchange [11,12], the oxidation of pollutants to safe by-products in liquid medium by highly reactive species has shown great promise. Advanced oxidation processes (AOPs), which are based on generation of highly reactive intermediates, are capable of oxidizing organic substrates. These reactive species, for example hydroxyl radicals ($\cdot\text{OH}$), can oxidize a broad range of pollutants fast and almost without selectivity. The non-thermal plasma technique is an AOP that combines different physical and chemical effects, such as pyrolysis, UV photolysis, electrohydraulic cavitation, as well the formation of oxidizing species: radicals (H , O , $\cdot\text{OH}$) and molecules (H_2O_2 , O_3 , etc.) [13,14]. Atmospheric pressure non-thermal plasma recently has attracted a lot of attention for the application of wastewater treatment due to its excellent performance in attacking organic pollutants and the absence of secondary pollution [6,13]. There are many different methods of non-thermal plasma generation, e.g.: DC plasma above liquid, pulsed streamer discharge in liquid, and dielectric barrier discharge. Among various plasma reactors for water treatment, glow discharge above water is attractive as an AOP because of the simplicity of the setup, the easy control of plasma parameters

and the possibility of generating discharge in different gases. Moreover, plasma treatment can be combined with other AOPs. The main problem with using plasma as an AOPs is its energy cost. The average destruction efficiency of plasma is in the range of 0.03-12 g kWh⁻¹ [15], which is still too high for wide use of this promising technology. One way to overcome this limitation is the use of plasma in combination with a catalyst, where the catalyst is activated directly by plasma, *e.g.* through UV photons. The combination of glow discharge with other advanced oxidation processes has been suggested as a tactical way to overcome the limitations of the plasma-chemical degradation process on its own. In this study, we have used DC glow discharge for the degradation of a widely used textile dye. This technique is coupled with photocatalysis with titanium dioxide (TiO₂). TiO₂ is used in mineralization of toxic organic pollutants in wastewater treatment. TiO₂ in solution can be excited by light of a wavelength less than 385 nm and [•]OH generated on the surface of the TiO₂ is able to oxidize non-selectively a great number of organic pollutants in water, as demonstrated in [16,17]. Chemical photodegradation processes occur through different pathways involving electron transfer, such as the excitation of the dye molecules adsorbed on the TiO₂ surface [18]. TiO₂ has an appropriate energy gap, which can be surpassed by the energy of solar photons. The energies of conduction and valence bands of TiO₂ are 3.1 and 0.1 V respectively, which means that the energy required for TiO₂ activation is 3.2 eV, so photoactivation of TiO₂ can be achieved by light absorption in the near UV range (<385 nm) [18]. When aqueous TiO₂ suspension is irradiated with light whose energy is higher than the energy gap of the semiconductor, conduction band electrons (e_{cb}⁻) and valence band holes (h_{vb}⁺) are formed. The photogenerated electrons will react with an adsorbed O₂ molecule, reducing it to the superoxide radical anion O₂^{•-}, and the photogenerated holes can directly oxidize the organic molecules [19,20]. The generalized reaction mechanism of the photocatalytic oxidation of organic molecules (RH) can be presented as set of Reactions 1-5. RH will degrade by losing one carbon atom by releasing CO₂, with potential intermediates of the aldehyde RCHO or the carboxylate RCOO⁻ [19].



Glow discharge plasma at atmospheric pressure is well known as a source of UV radiation [21] due to the presence of the OH band (286-315 nm), NO band (260-280 nm) and N₂ band (320 nm-450 nm) in the emission spectrum. Accordingly, the coupling of the non-thermal plasma of DC discharge with TiO₂ can be highly effective for the degradation of the dye.

The objective of this work is to study the degradation of Acid Blue 25 dye (AB25), used in the textile industry, by DC glow discharge generated in argon atmosphere in the absence and presence of TiO₂. The effect of operational parameters such as initial dye concentration, pH and catalyst load on the degradation of AB25 is investigated.

2 Experimental procedure

2.1 Materials

Acid Blue 25 (abbreviation: AB25; C.I. number: 62055; chemical class: anthraquinone; molecular formula: C₂₀H₁₃N₂NaO₅S, 1-amino-9,10-dihydro-9,10-dioxo-4-(phenylamino)-2-anthracenesulfonic acid, monosodium salt) is used as a model compound for plasma AOP. The chemical is purchased from Sigma Aldrich and is utilized as received. The aqueous solution of AB25 is prepared by dissolving the required quantity in distilled water. The pH of the solution is adjusted using sodium hydroxide (NaOH) or sulfuric acid (H₂SO₄). The conductivity and pH of the solution are measured by a conductivity meter (DDS-11A) and a pH meter (pHSJ-3F), respectively. All reagents utilized in the present work are purchased among the products of high purity.

2.2 Experimental setup

The scheme of the reactor is shown in Fig. 1. The reactor chamber is a cylindrical vessel with a diameter of 100 mm and height of 150 mm. The DC discharge system consists of a high voltage power supply connected through a ballast resistor to the reactor chamber. The power supply can provide a voltage of 15 kV and current at the range of 0-100 mA. The polarity of the HV electrode is positive through all the experiments. A cone-shaped stainless steel metal electrode with a top angle of approximately 40° and a rounded, polished tip is attached to a micrometer screw above the liquid reservoir. The distance between

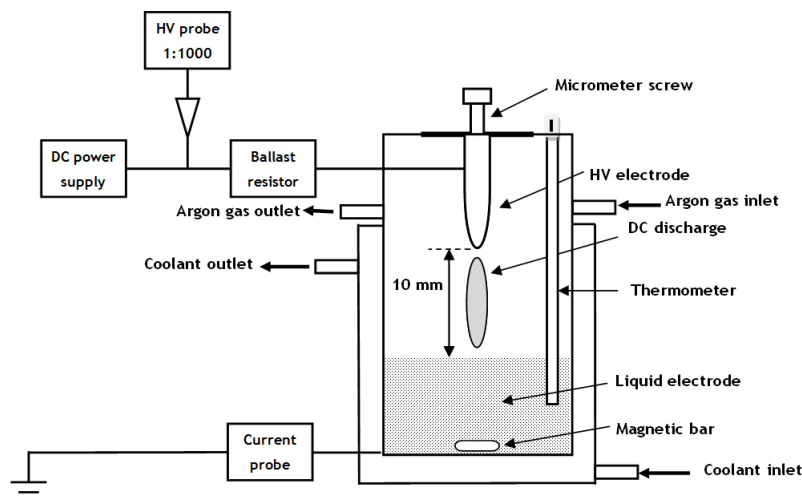


Figure 1: The scheme of the reactor of glow discharge above water used for AB25 degradation with Ar gas flow.

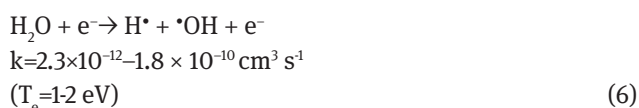
the electrode and the water surface can be adjusted with the micrometer screw with a precision of 0.1 mm. In all experiments, this distance is fixed to 10 mm and treatment is carried out for 2 hours. The glow discharge degradation of AB25 is studied in the reactor for a constant solution volume of 500 mL, while stirring the liquid medium in order to achieve a uniform treatment of the whole volume. The efficiency of the discharge has been examined by measuring the decolorization of the dye solution with a UV/VIS spectrophotometer UV mini-1240 “SHIMADZU”, (SBN –SPEC-91). The concentration of the dye was determined from the measured UV–VIS spectrum, using the maximum of AB25 absorption at 602 nm.

In the present study, plasma is generated in the closed reactor chamber, where argon gas is pumped through at flow rate of 300 sccm. Before the start of each experiment, the system has been purified with argon flow of 1 sLm for 10 minutes, in order to remove residual air from the chamber. The use of argon provides a controllable atmosphere where side reactions with formation of HNO_3 , various oxides N_xO_y and HNO_2 are strongly suppressed. This makes interpretation of results simpler and also excludes any effect of HNO_3 as a strong acid on the stability of TiO_2 . It has to be noted that air dissolved in water has not been removed prior to the experiments. Correspondingly, some traces of N_2 and O_2 coming from the dissolved in water air can be observed, but their effect on AB25 destruction is very low and can be neglected. Indeed, it was observed that liquid conductivity is increased during the treatment but this effect is very low compared to the same discharge working in ambient air. For example, we observed an increase of the conductivity from $50 \mu\text{S cm}^{-1}$ to

$125 \mu\text{S cm}^{-1}$ after 120 minutes of treatment. With glow discharge working in the ambient air at the same current, the final conductivity is much higher (about 4.2 mS cm^{-1}). In our opinion, the observed small increase of the conductivity is because of dissolved N_2 in water but it is still low and does not affect the discharge properties.

3 Results and discussion

The principal oxidative species formed in gas phase by the discharge are oxygen atoms (O), hydroxyl radicals ($\cdot\text{OH}$) and hydrogen peroxide (H_2O_2) [22]. The dominant reactions which take place in the plasma-liquid interface are listed as follows [23,24]:



When glow discharge is generated in Ar, the $\cdot\text{OH}$ radicals can also be produced through dissociative excitation of H_2O by excited Ar atoms. It was suggested that reaction

with Ar^* is the main pathway for the formation of $\cdot\text{OH}$ radicals in argon-water vapor mixtures [24]:



Many authors [20–22] have studied the influence of the gas atmosphere during removal of phenol using an electric discharge. They concluded that the use of argon results in negligible production of atomic oxygen and ozone, so here in this experiment, $\cdot\text{OH}$ and H_2O_2 probably contribute mainly to the degradation of pollutants.

3.1 Plasmachemical treatment without TiO_2

3.1.1 Effect of initial dye concentration

The effect of initial dye concentration C_0 varying from 10 to 50 mg L^{-1} on the AB25 degradation by glow discharge is investigated by measuring the kinetics of AB25 decolorization. Typical examples of kinetics are plotted in Fig. 2.

The initial pH value of the treated samples with different amounts of the dye is fixed at a constant value of 6.7. For all initial dye concentrations, exponential decay of AB25 is observed during treatment, which can be described well with first-order reaction kinetics. The plasma efficiency is calculated as the initial rate of AB25 destruction ($dC_{\text{H}_2\text{O}_2}/dt$), as suggested in [25]. The initial destruction rate $dC_{\text{H}_2\text{O}_2}/dt$ at dye concentrations of 10, 30, 40 and 50 mg L^{-1} is calculated to be 0.224, 0.573, 0.664 and 0.723 $\text{mg L}^{-1} \text{ min}^{-1}$, respectively. According to our experimental results, the initial degradation rate increased with the increase of dye concentration, which is in good agreement with results described by other authors [26].

3.1.2 Effect of pH

The degradation of AB25 by DC glow discharge at initial dye concentration of 20 mg L^{-1} is studied for different pH values from 2 to 10.3. The obtained initial degradation rates at these pH values are shown in Fig. 3.

The rate of AB25 degradation strongly depends on the pH of the solution. The degradation rate in acidic solutions (2–4.3) is higher, especially at pH 2, and decreases to 0.38 mg/l min with an increase of pH from 2 to 5.65. A similar effect is observed in basic media, where higher degradation rate is found at a pH of 10.3. In order to confirm that the pH value has no effect on the UV/Vis

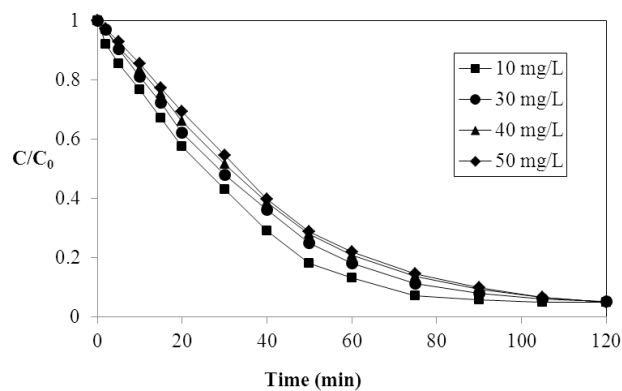


Figure 2: Kinetics of AB25 decolorization (absorption at 602 nm) by glow discharge in Ar atmosphere for different initial dye concentrations (treated volume 500 mL; initial dye concentration in the range of 10–50 mg L^{-1} ; pH of 6.7).

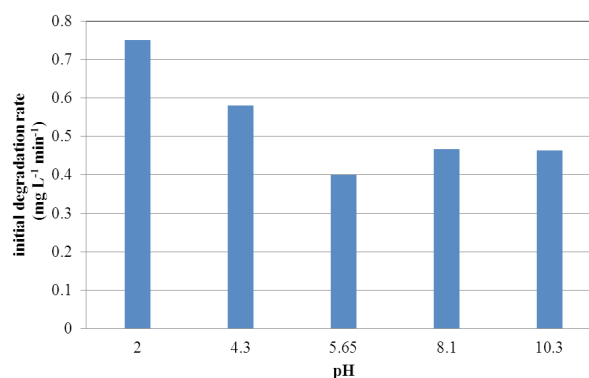


Figure 3: Initial degradation rate at various pH values (treated volume 500 mL; initial dye concentration: 20 mg L^{-1}). No TiO_2 catalyst is added.

absorbance curves of AB25, an additional experiment has been carried out. The results indicate that changing the initial pH of the dye solution has no effect on the maximum of AB25 absorption in the range of pH from 2 to 10.3. This means that the faster degradation in strong acidic conditions is probably associated with protonation of the negatively charged SO_3^- group and a higher oxidation potential of $\cdot\text{OH}$ radicals generated by plasma at low pH. The increase of degradation rate in basic media may be caused by the change in the hydrophobic property of the dye, as suggested in [27], where the authors investigated the degradation of Acid Blue 25 by 1700 kHz ultrasonic irradiation. They have found that the initial bleaching rate in acidic solutions is higher, especially at pH 1.4, and decreases from pH 1.4 to 5.7, which agrees with our results. We also recently obtained similar results in [28] for the degradation of Acid Blue 25 in aqueous medium by direct UV irradiation.

3.2 Plasmacatalytic process

Combination of plasma with a photocatalyst is considered as a possible way to enhance the degradation of organic pollutants in liquids and to decrease energy costs of the process [29]. In the present work, we studied the combination of the non-thermal DC glow discharge with TiO_2 for AB25 destruction. The glow discharge is a source of UV photons mostly because of the presence of the OH (A-X) band in the range of 286–315 nm, as shown in the emission spectrum of the discharge at 20 mA presented in Fig. 4. UV photons can activate the TiO_2 catalyst, which should lead to higher dye destruction efficiency. The treatment efficiency in the presence of a catalyst depends on several parameters, including the pH of the solution, the catalyst load, the nature of the substance, etc. In some investigations, it has been shown that increasing the TiO_2 load above an optimal value will affect the catalyst surface that is exposed to the UV light, which prevents the excitation light from reaching it [30] and so causes the overall efficiency to decrease.

3.2.1 Determination of the optimal concentration of TiO_2

The determination of the optimum catalyst concentration is carried out by varying the catalyst load for the AB25 destruction process with all other parameters fixed. Fig. 5 represents the reduced AB25 concentration C/C_0 with $C_0 = 20 \text{ mg L}^{-1}$ for TiO_2 concentrations from 0 to 1 g L^{-1} . The small difference in the C/C_0 value after 120 min in between results presented on Fig. 2 for AB25 destruction with $C_0 = 30 \text{ mg L}^{-1}$ and on Fig. 5 for the case without TiO_2 can be explained by the fact that control of the discharge power is possible with 2–5% precision and so observed difference is in the limit of experimental error. The results show that the degradation increased with treatment time until the load reaches 0.5 g L^{-1} . The maximum of degradation (90%) is obtained within 1 h of treatment. On the other side, the plasmachemical treatment without catalyst gave only 78% AB25 degradation during the same treatment time. Beyond this optimal catalyst concentration, the treatment efficiency decreases. These results show that for any concentration higher than 0.5 g L^{-1} , other factors can affect the degradation. Probably, increasing the TiO_2 concentration leads to the aggregation of the catalyst particles reducing the contact surface between the solution and catalyst. This decreases the number of active sites on the surface, making the UV activation of TiO_2 difficult and resulting in a loss of catalyst efficiency.

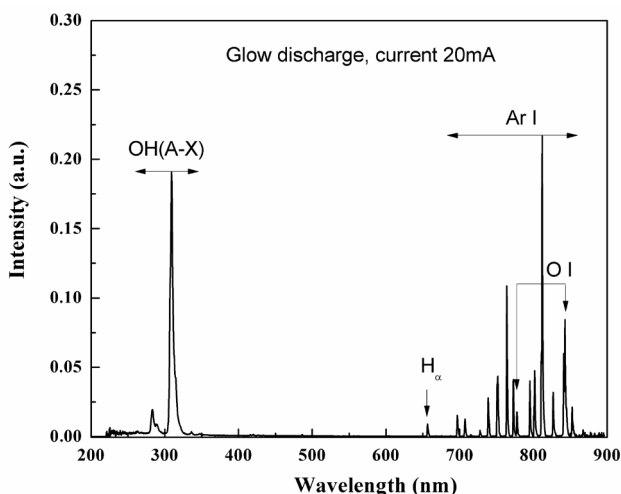


Figure 4: Optical emission spectrum of the glow discharge at 20 mA generated above water in Ar atmosphere.

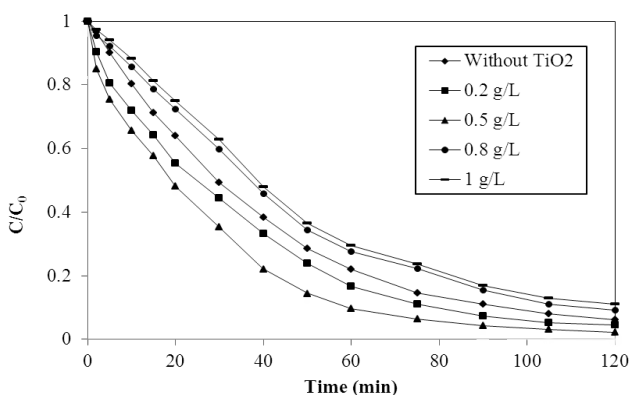


Figure 5: Kinetics of AB25 degradation process for different initial concentrations of TiO_2 (treated volume 500 mL; initial dye concentration 20 mg L^{-1} ; pH 6.7).

3.2.2 Effect of pH

TiO_2 has an optimal pH where the best performance of the catalyst can be achieved. This optimal pH value depends on the solution temperature, catalyst structure and solution composition. In order to investigate the influence of initial pH on AB25 degradation by DC glow discharge in the presence of 0.5 g L^{-1} of TiO_2 , the experiments were carried out at different solution pH values adjusted by H_2SO_4 and NaOH admixing. The results are shown in Fig. 6. AB25 degradation by DC glow discharge in the presence of TiO_2 is enhanced at low pH and monotonically decreases with an increase of the solution pH to 10. This behavior is different than the observed case of treatment without catalyst, where an increase of efficiency of AB25 degradation is observed at low as well as high pH. This fact leads to the conclusion that the best performance of the

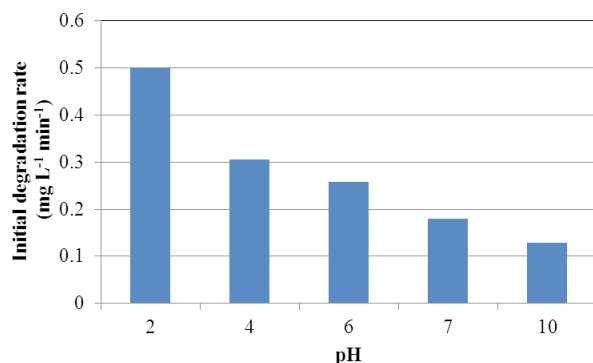


Figure 6: Initial degradation rate of AB25 at various pH values in the presence of 0.5 g L⁻¹ of TiO₂ (treated volume 500 mL, initial dye concentration 20 mg L⁻¹).

plasma reactor with catalyst TiO₂ can be achieved only at low pH. Therefore, it may be desirable to work in ambient air atmosphere instead of in argon, because of HNO₃ and HNO₂ production in the solution during treatment. HNO₃ and HNO₂ formation will lead to an artificial decrease of pH and so will enhance the photocatalyst process efficiency. Nevertheless, investigation of reactor operation in ambient air is out of scope of the present study.

4 Conclusion

Non-thermal glow discharge at atmospheric pressure is used as AOP to decompose the widely used Anthraquinonic dye Acid Blue 25 in liquid medium. The process is carried out with and without photocatalyst TiO₂ in order to combine the plasma effect with TiO₂ activation by UV radiation from the discharge. It was found that the efficiency of AB25 destruction can be controlled by solution pH and depends on the initial dye concentration. The higher the initial AB25 concentration, the higher the initial destruction rate is. The pH has significant influence on the dye degradation and fast AB25 destruction is observed at pH < 3. The degradation rate is increased in the presence of TiO₂, in comparison to discharge alone. As shown by the results, the degradation increases with treatment time until the catalyst load reaches 0.5 g L⁻¹. The degradation maximum (90%) is obtained within 1 h of treatment, while the plasmachemical treatment without catalyst only gave 78% AB25 degradation after the same treatment time. Beyond this optimal catalyst concentration, a reduction in the treatment efficiency is observed.

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